

The pressure-amorphized state in zirconium tungstate: a precursor to decomposition

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Abstract

In contrast to widely accepted view that pressure-induced amorphization arises due to kinetic hindrance of equilibrium phase transitions, here we provide evidence that the metastable pressure-amorphized state in zirconium tungstate is a precursor to decomposition of the compound into a mixture of simple oxides. This is from the volume collapse ΔV across amorphization, which is obtained for the first time by measuring linear dimensions of irreversibly amorphized samples during their recovery to the original cubic phase upon isochronal annealing up to 1000 K. The anomalously large ΔV of $25.7 \pm 1.2\%$ being the same as that expected for the decomposition indicates that this amorphous state is probably a precursor to kinetically hindered decomposition. A P – T diagram of the compound is also proposed.

1. Introduction

At high pressure many materials exhibit structural phase transitions, while some become amorphous [1–7]. Although it is widely believed that the phenomenon of pressure-induced amorphization (PIA) arises due to kinetic hindrance of equilibrium phase transitions, the structure of the equilibrium high-pressure phase, which the compound should have ideally evolved to, has remained speculative or unknown in most cases. Only in a few systems such as ice [1], quartz [2] and tetra-cyano-ethylene [8] can the high-pressure phase be identified from further measurements [9] and from computer simulations [10]. In this context, in addition to characterization of the p -amorphized state using x-ray diffraction and Raman spectroscopy, measurements of additional structural properties/features of this state such as its volume can be helpful in the identification of the equilibrium phase among different high-pressure polymorphs. The volume change across structural phase transitions is easily quantified from

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the measurement of the lattice parameter. If the phase transition is irreversible, studies on the recovered samples can also yield this information. On the other hand, across amorphization a reliable estimate of volume change is difficult to obtain from x-ray diffraction due to the absence of sharp diffraction peaks in the disordered state. Earlier, a large-volume piston–cylinder apparatus was used for obtaining ΔV across amorphization in ice [1] and across the transformation of low-density a-SiO₂ to high-density a-SiO₂ [5]. Here we obtain the volume collapse ΔV across the irreversible pressure-induced amorphization in zirconium tungstate ZrW₂O₈, a material with large isotropic negative thermal expansion [11–14], from the linear dimension of the *p*-amorphized samples during isochronal annealing leading to the crystallization to the original cubic structure. The equilibrium state, which the system should have ideally evolved to, is identified from the magnitude of ΔV . A *P*–*T* diagram showing stable and metastable phases of the compound is also proposed.

2. Experimental details

In order to obtain the volume collapse the sample underwent during amorphization, we measured the longest dimension of the sample during cumulative isochronal annealing of *p*-amorphized zirconium tungstate platelets obtained by pressure soaking the samples to 5 GPa for about 2 h. Pressure treatment was carried out in a Bridgman opposed-anvil (diameter 30 mm) high-pressure device consisting of a 500 ton hydraulic press with an electrically operated pump [15]. Granular sample powder, placed in a thin-walled (7.5 μ m) stainless-steel capsule of 5 mm diameter and 0.5 mm height, was mounted inside a pyrophyllite gasket, with steatite as the pressure-transmitting medium, and compressed to the desired pressure. Although amorphization is reported to occur at 2.2 GPa under hydrostatic conditions [14], we found incomplete amorphization at pressures lower than 5 GPa. In a single pressure treatment run, about 20 mg of sample could be loaded. In most of the pressure treatment runs the recovered sample was in the form of a platelet with lateral dimensions ranging between 2 and 5 mm and thickness of about 0.3 mm, while in some other runs the sample was fragmented into several small pieces. All annealings were carried out for 30 min in air. Dimension measurements were made at ambient temperature using an optical microscope of magnification 50 \times equipped with cross-wires and a calibrated *X*–*Y* translation stage of least count 10 μ m. This method of measurement of the change in size has the advantage that it avoids errors arising from the porosity, if any, of the as-synthesized samples.

3. Results and discussion

Annealing the samples at higher temperatures resulted in a substantial increase in their linear dimensions. Figure 1 shows the longest dimension of the samples, normalized to that after annealing at 1000 K, as a function of annealing temperature. Note that a large increase in sample dimension takes place above 870 K. In order to identify this state of the sample we recorded the x-ray diffraction pattern after annealing the sample to 1000 K. For recording the diffraction patterns the platelet sample was ground into fine powder and spread uniformly over a zero-background sample holder made of $\langle 911 \rangle$ cut silicon single crystal. Figure 2 shows the x-ray diffraction pattern of the annealed sample along with those of as-synthesized and *p*-amorphized samples obtained using Cu K α radiation. Note that there is a complete correspondence between the diffraction peaks of 1000 K annealed and the as-synthesized samples, indicating that the amorphous sample crystallized back to the original cubic phase upon annealing. Furthermore, the annealed sample does not show new/additional peaks. Note that the difference curve goes negative on either side of the centre of the strongest (210) peak. This is because of the slightly

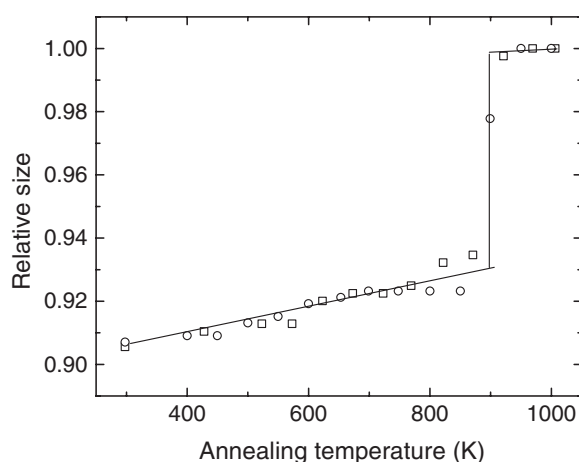


Figure 1. The longest linear dimension of p -amorphized ZrW_2O_8 samples after cumulative isochronal annealing to successively higher temperatures. The data presented here are from independent annealing experiments on separate samples and are normalized with respect to the sizes after annealing at 1000 K. Sample A: \circ ; sample B: \square . Note the large increase in sample length above 870 K. The lines drawn through the points are guides to the eye.

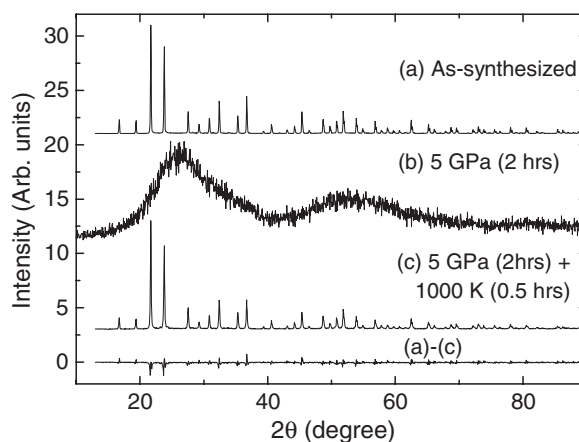


Figure 2. Powder x-ray diffraction patterns of ZrW_2O_8 samples obtained using $\text{Cu K}\alpha$ radiation at ambient temperature and pressure after different pressure–temperature treatments. (a) As-synthesized, (b) after pressure soaking for 2 h at 5 GPa and (c) after cumulative isochronal annealing of the p -treated sample to 1000 K. The broad diffraction pattern in (b) arises due to amorphous nature of the p -treated sample. The diffraction peaks at large 2θ appear as a doublet due to the $\text{K}\alpha_1$ and $\text{K}\alpha_2$ wavelengths. The intensities of the patterns (a) and (c) are normalized with respect to those of the strongest (210) peak at 21.7° . For comparison, the (a)–(c) difference plot is also given.

larger width of the diffraction peak for the 1000 K annealed sample. The small difference in intensity of the other peaks, between the as-synthesized and the annealed samples, as seen in the difference plot, could be due to either a marginal positional disorder or a preferred orientation.

The annealed sample was further characterized using Raman spectroscopic measurements in the back-scattering geometry using the 488 nm line of an argon ion laser, using a set-up described elsewhere [16]. Figure 3 compares the Raman spectrum of the annealed sample with

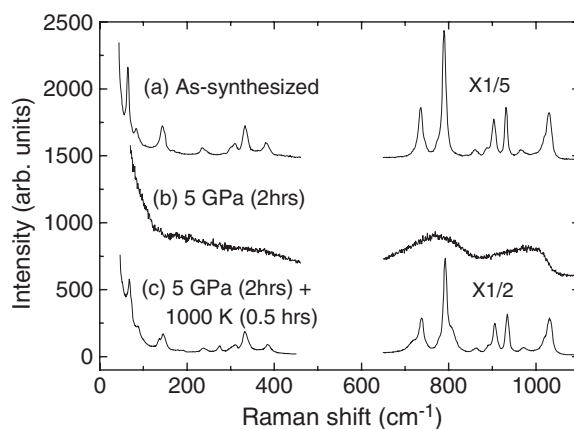


Figure 3. Raman spectra of ZrW_2O_8 samples at ambient temperature and pressure after different pressure–temperature treatments. (a) As-synthesized, (b) after pressure soaking for 2 h at 5 GPa and (c) after cumulative isochronal annealing of the p -treated sample to 1000 K. The broad bands in the spectrum (b) in the ν_1 – ν_3 internal mode region of the tungstate ion arise due to the amorphous nature of the p -treated sample.

those of as-synthesized and p -amorphized samples. One can clearly see that the spectrum of the annealed sample has all the peaks of the as-synthesized ZrW_2O_8 confirming the recovery to the original cubic phase. However, in addition a weak peak at 272 cm^{-1} and a few weak shoulders at 136 , 712 and 810 cm^{-1} are found. As the x-ray diffraction pattern does not show any additional lines, the possibility of the new Raman features arising from other coexisting phase/phases can be ruled out. It may be mentioned here that an orientational disorder of polyatomic units/ions is known to result in the presence of more Raman lines than expected from group theory [17]. The structure of zirconium tungstate consists of interpenetrating sublattices of zirconium cations and tungstate anions, and its high-temperature phase has been reported to have oxygen disorder leading to two configurations of tungstate ions [18]. Hence the additional peaks may be attributed to the existence of some amount of residual orientational disorder of tungstate ions in the annealed samples. The disorder may also cause changes in the intensities of the diffraction peaks. These results thus suggest a nearly complete recovery to the original cubic phase upon annealing.

As the annealing at 1000 K resulted in recovery to the original cubic structure, one can estimate from the dimension of the annealed sample the extent of irreversible linear compression the sample had undergone during amorphization. We obtain this from the ratio of the size L of the unannealed (amorphous) sample to that, L_0 , after annealing to 1000 K. From the data (figure 1) the linear compression L/L_0 turns out to be $0.906(5)$. Considering the amorphous phase to be isotropic, the volume compression V/V_0 then becomes $0.743(12)$, where V and V_0 are the volumes in the amorphous and the cubic phases respectively. This implies that the irreversible volume collapse $\Delta V_A/V_0 = 1 - V/V_0$ upon amorphization relative to the cubic phase is as large as $25.7 \pm 1.2\%$. A large change in the volume is also evident from the corresponding shift of the main peak of the amorphous sample to larger 2θ with respect to the two main peaks in the cubic phase. It may be mentioned that this material undergoes an intermediate cubic (α) to orthorhombic (γ) transition at 0.3 GPa prior to amorphization, which is also irreversible [19]. Among the known examples of high-pressure phase transitions, the volume collapse in the present case is anomalously large. Considering the present amorphous state to be metastable, we need to identify the final state, which this

compound should have ideally evolved to, had the kinetics been adequate. In this context it is worth examining the present results in the light of a recent unified model of pressure-induced amorphization and decomposition [7]. According to this ‘PIA could also occur if an equilibrium decomposition of the compound to more dense-packed daughter compounds is kinetically constrained’. An increase in temperature can provide sufficient kinetics for the decomposition to proceed. Several systems such as Fe_2SiO_4 , CuGeO_3 and Mg_2SiO_4 that are known to decompose under high-pressure–high-temperature conditions have been found to exhibit PIA at ambient temperature [3]. In view of the fact that ZrW_2O_8 can be synthesized from stoichiometric mixtures of ZrO_2 and WO_3 by sintering at high temperature, we consider the mixture of individual oxides as one of the possible decomposition routes. We calculate the volume change ΔV_D upon decomposition of the compound according to the reaction $\text{ZrW}_2\text{O}_8 \rightarrow \text{ZrO}_2 + 2\text{WO}_3$ from the unit cell volume data of ambient pressure phases of the parent and the daughter compounds. Using $\Delta V_D = V_0 - (V_1 + 2V_2)$, where V_1 and V_2 are the volumes per formula unit of the daughter compounds ZrO_2 and WO_3 respectively, we get $\Delta V_D/V_0 = 0.267$. Note that $\Delta V_A = \Delta V_D$ within experimental error, i.e., the measured value of the volume collapse across the amorphization is the *same* as that expected for decomposition. It may be pointed out that $\Delta V_A/V_0$ is quite different from that for the formation of a hexagonal phase of ZrW_2O_8 (reported fractional volume change ~ 0.42 [20]) under different P – T conditions. This strongly suggests that the amorphous phase may be treated as a precursor to the decomposed state; however, one does not expect macroscopic growth of the individual daughter phases (disordered assemblage) to take place at ambient temperature. In view of this, one can view the amorphous phase as that of ‘microscopically mixed’ daughter compounds. One could in principle carry out a more rigorous calculation [21, 22] of ΔV as a function of pressure by taking into account the equations of state of the parent and the daughter compounds; however, as the volume change is very large in the present case, conclusions drawn from the ambient pressure data are also valid. The large magnitude of the volume collapse across amorphization in ZrW_2O_8 arises because its cubic phase can also be viewed as a loosely packed corner-linked network structure of WO_4 tetrahedra and ZrO_6 octahedra. On the other hand, the daughter compounds are very densely packed.

We now discuss a P – T diagram of this technologically important, but metastable material. Zirconium tungstate is stable only between 1380 and 1505 K and it decomposes, if cooled slowly, into a mixture of constituent oxides. However, the metastable cubic phase can be quenched to the ambient and decompose only when heated above 1173 K. In addition to the pressure-induced phase transition to the γ - ZrW_2O_8 phase [23] and subsequent amorphization [14], this compound also exhibits an order–disorder (α – β) transition at 428 K and ambient pressure [18]. Amores *et al* [24] have found, from x-ray diffraction measurements on recovered samples after high-pressure–high-temperature treatments, that it transforms to the γ -phase at 0.6 GPa–873 K, turns amorphous at 1 GPa–873 K and decomposes into a mixtures of oxides at 0.6 GPa–1073 K. On the other hand, under different P – T conditions, i.e., 1.4 GPa–897 K and 2.2 GPa–1042 K, a hexagonal phase of ZrW_2O_8 has also been reported [20]. Thus the present results, along with those reported earlier, show the existence of three different paths of evolution of p -amorphized samples: (a) complete recovery to cubic structure upon annealing if pressure is released, (b) formation of hexagonal phase under high pressure and moderate temperatures and (c) decomposition of the compound at high pressure and relatively high temperatures. On the basis of these results as a function of pressure and temperature, we propose a P – T diagram for ZrW_2O_8 , in figure 4. The negative slope of the amorphization boundary is understandable because a moderate increase in temperature can increase the kinetics slightly and the onset of pressure-induced structural change (amorphization) can occur at a lower pressure. This has been found experimentally

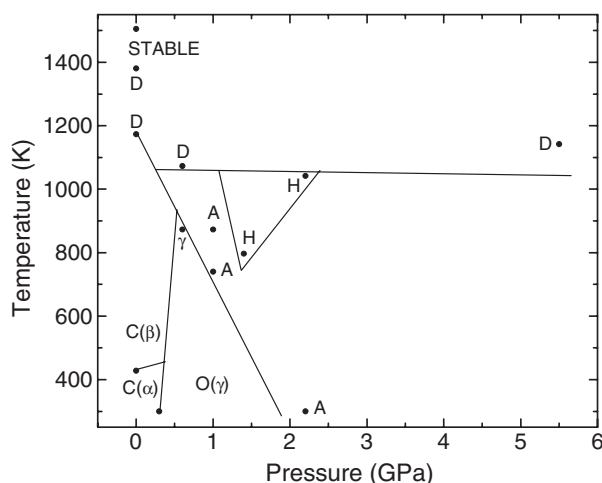


Figure 4. The proposed P - T diagram of ZrW_2O_8 . A: amorphous [14, 24]; D: decomposed state [20, 24]; H: hexagonal phase [20]; C(α): cubic α -phase [11]; C(β): cubic β -phase [18]; O(γ): orthorhombic γ -phase [23]. The solid lines are the proposed phase boundaries.

also [20]. This P - T diagram is not a phase diagram in the strict sense (a phase diagram is supposed to show only the equilibrium phases); however, it is useful as it identifies the regions of existence of different metastable phases from the point of view of applications. More measurements are required as a function of pressure and temperature to delineate the phase boundaries more precisely. Theoretical phase diagrams based on total energy calculations [25], not available for ZrW_2O_8 so far, are also desirable as these would throw further light on the phenomena of pressure-induced amorphization and decomposition in this system. Compounds that undergo irreversible amorphization have often exhibited polyamorphism [26], i.e., the existence of low- and high-density amorphous phases, such as those in quartz [5] and ice [27]. It would be interesting to investigate whether this compound also exhibits polyamorphism.

4. Conclusions

To conclude, the volume collapse across amorphization is obtained from the measurement of the linear dimensions of irreversibly p -amorphized samples of zirconium tungstate during their recovery to the original cubic phase upon isochronal annealing. The value of the volume collapse across the amorphization is found to agree very well with that expected for a decomposition of the compound. This strongly suggests that the final state, which the system would have ideally evolved to, is perhaps a mixture of ZrO_2 and WO_3 . In view of this, the metastable p -amorphized state may be considered as a precursor to kinetically hindered decomposition rather than a phase transition. The present results also motivate the examination of other compounds and minerals that exhibit PIA from the alternative point of view of a possible decomposition.

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